

## Claims

1. A compound of the formula  $\text{ROC}_6\text{H}_4\text{SO}_2\text{NMSO}_2\text{R}_f$  where R is a  $\text{C}_1\text{-C}_5$  alkyl,  $\text{R}_f$  is a  $\text{C}_1\text{-C}_8$  perfluoroalkyl, Li, Na, H, and K, and M is selected from the group consisting of  
5 H, Li, K, Na,  $\text{R}'_3\text{NH}^+$ , or mixtures thereof, where  $\text{R}'$  is a  $\text{C}_1\text{-C}_5$  alkyl.
2. A compound of the formula  $\text{ROC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f$  where R is a  $\text{C}_1\text{-C}_5$  alkyl and  $\text{R}^1$  is selected from the group consisting of Li, H, K and Na, and  $\text{R}_f$  is a  $\text{C}_1\text{-C}_8$  perfluoroalkyl.
- 10 3. A sulfonimide bearing compound of the formula  $\text{HOC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f$  where  $\text{R}^1$  is selected from the group consisting of Li, K, H, and Na, and  $\text{R}_f$  is a  $\text{C}_1\text{-C}_8$  perfluoroalkyl.. comprising,  
reacting  $\text{ROC}_6\text{H}_4\text{SO}_2\text{Cl}$  where R is a  $\text{C}_1\text{-C}_5$  alkyl with  $\text{R}_f\text{SO}_2\text{NH}_2$  where  $\text{R}_f$  is any  $\text{C}_1\text{-C}_8$  perfluoroalkyl, and a base selected from the group consisting of Trimethylamine,  
15 Triethylamine, Pyridine, Imidazole, Pyrimidine or mixtures thereof in the presence of a first solvent selected from the group consisting of Acetone, Acetonitrile, N,N-dimethylacetamide, N,N-dimethylformamide, Dimethyl sulfoxide, Hexamethylphosphoramide, Nitromethane, Pyridine, Tetrahydrofuran or mixtures thereof to produce a first intermediate compound of the formula  $\text{ROC}_6\text{H}_4\text{SO}_2\text{NMSO}_2\text{R}_f$   
20 where M is  $\text{R}'_3\text{NH}^+$ , where  $\text{R}'$  is a  $\text{C}_1\text{-C}_5$  alkyl,  
reacting the first intermediate compound with an alkali metal salt selected from the group consisting of Lithium methoxide, Lithium ethoxide, Lithium tert-butoxide, Lithium phenolate, Lithium hydroxide, Sodium methoxide, Sodium ethoxide, Sodium tert-butoxide, Sodium phenolate, Sodium hydroxide Potassium methoxide, Potassium  
25 ethoxide, Potassium phenolate, Potassium tert-butoxide, Potassium hydroxide or mixtures thereof in the presence of a second solvent selected from the group consisting of Methanol, Ethanol, Isopropanol, tert-Butanol, Acetone, Acetonitrile, N,N-dimethylacetamide, N,N-dimethylformamide, Dimethyl sulfoxide,

Hexamethylphosphoramide, Nitromethane, Tetrahydrofuran or mixtures thereof to produce a second intermediate of the formula  $\text{ROC}_6\text{H}_4\text{SO}_2\text{NMSO}_2\text{R}_f$  where M is selected from the group consisting of Li, Na and K,  $\text{R}_f$  is a  $\text{C}_1\text{-C}_8$  perfluoroalkyl, and R is a  $\text{C}_1\text{-C}_5$  alkyl,

5        reacting the second intermediate with an alkali alkane thiolate selected from the group consisting of sodium ethane thiolate, lithium ethane thiolate, potassium ethane thiolate and mixtures thereof to produce a sulfonimide bearing compound of the formula  $\text{HOC}_6\text{H}_4\text{SO}_2\text{NMSO}_2\text{R}_f$ , where M is selected from the group consisting of Li, Na, H and K, and  $\text{R}_f$  is a  $\text{C}_1\text{-C}_8$  perfluoroalkyl.

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4. An alkali sulfonimide bearing compound of the formula  $\text{ROC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f$  where R and  $\text{R}^1$  are the same or different and each of R and  $\text{R}^1$  are selected from the group consisting of Li, Na, H, and K, and  $\text{R}_f$  is a  $\text{C}_1\text{-C}_8$  perfluoroalkyl.

15    5. The alkali sulfonimide bearing compound of claim 4 wherein R and  $\text{R}^1$  each are Na.

6. An amine terminated sulfonimide bearing compound of the formula  $\text{H}_2\text{NC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f$  where  $\text{R}^1$  is selected from the group consisting of Li, Na, H, and K, and  $\text{R}_f$  is a  $\text{C}_1\text{-C}_8$  perfluoroalkyl.

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7. The amine terminated sulfonimide bearing compound of claim 7 where  $\text{R}^1$  is Na.

8. A method of making an alkali phenoxy sulfonimide functionalized polyphosphazene comprising,

25        reacting a polyphosphazene of the formula  $(\text{N}(\text{PCl}_2)_n$ , where  $n \geq 3$  with an alkali oxide derivative selected from the group consisting of sodium p-methyl phenoxide, lithium p-methyl phenoxide, potassium p-methyl phenoxide to produce a first intermediate of the formula  $[(\text{NP}(\text{Cl})_x(\text{OC}_6\text{H}_4)_{2-x})_n]$ , where  $n \geq 3$ ,

reacting the first intermediate with a second alkali salt  $R^1OC_6H_4SO_2NR^1SO_2R_f$ , where  $R^1$  is Li, K, or Na, and where  $R_f$  is a  $C_1$ - $C_8$  perfluoroalkyl, to produce a second intermediate of the formula such as

$[NP(OC_6H_4SO_2NR^1SO_2R_f)_x(OC_6H_4CH_3)_y(Cl)_{2-x-y}]_n$ , where  $R^1$  is Li, Na, or K, and

where  $R_f$  is a  $C_1$ - $C_8$  perfluoroalkyl.

reacting the second intermediate with a third alkali salt selected from the group consisting of  $H_3CC_6H_4ONa$ ,  $NaOC_6H_5$ ,  $NaOC_6H_4CF_3$ ,  $LiOC_6H_4CH_3$ ,  $LiOC_6H_5$ ,  $LiOC_6H_4CF_3$ ,  $H_3CC_6H_4OK$ ,  $KOC_6H_5$  and  $KOC_6H_4CF_3$  to produce an alkali phenoxy sulfonimide functionalized polyphosphazene of the formula such as

$[NP(OC_6H_4SO_2NR^1SO_2R_f)_x(OC_6H_4CH_3)_{2-x}]_n$ , where  $R_f$  is a  $C_1$ - $C_8$  perfluoroalkyl, and where  $R^1$  is Li, K or Na.

10. The method of claim 9 wherein  $R^1$  is Na.

11. A method of making a phenoxy sulfonimide functionalized polyphosphazene comprising,

reacting polyphosphazene of the formula  $(NPCl_2)_n$ , where  $n \geq 3$  with  $R^1OC_6H_4CH_3$  and  $R^1OC_6H_4SO_2NR^1SO_2R_f$  where  $R^1$  is selected from the group consisting of Na, K and Li and  $R_f$  is a  $C_1$ - $C_8$  perfluoroalkyl, to produce a reaction product, and reacting the reaction product with  $R^1OC_6H_4CH_3$  where  $R^1$  is selected from the group consisting of Na, K, H and Li to produce an alkali phenoxy sulfonimide functionalized polyphosphazene of the formula  $[NP(OC_6H_4SO_2NR^1SO_2R_f)_x(OC_6H_4CH_3)_{2-x}]_n$ .

12. The method of claim 11 wherein  $R^1$  is Na.

13. A sulfonimide functionalized polyphosphazene homopolymer of the formula  $[NP(OC_6H_4SO_2NR^2SO_2R_f)_2]_n$  where  $R^1$  is selected from the group consisting of Li, Na, H and K.

14. The homopolymer of claim 13 wherein R<sup>1</sup> is Na.

15. A method of manufacture of a sulfonimide functionalized polyphosphazene homopolymer of the formula  $[NP(OC_6H_4SO_2NR^1SO_2R_f)_2]_n$  where R<sup>1</sup> is selected from the group consisting of Li, Na, H, and K and , R<sub>f</sub> is a C<sub>1</sub>-C<sub>8</sub> perfluoroalkyl, comprising, reacting (NPCL<sub>2</sub>)<sub>n</sub>, where n ≥ 3 with R<sup>1</sup>OC<sub>6</sub>H<sub>4</sub>NR<sup>1</sup>SO<sub>2</sub>R<sub>f</sub> where R<sup>1</sup> is selected from the group consisting of Li, K and Na and , R<sub>f</sub> is a C<sub>1</sub>-C<sub>8</sub> perfluoroalkyl, at a temperature of about 60 °C to about 200 °C at a pressure of about ambient to about 12 bar for about 12 hours to about 40 hours.

16. The method of claim 15 wherein R<sup>1</sup> is Na.

17. A phenoxy sulfonimide functionalized polyphosphazene copolymer of the formula  $[NP(ZR^2)_x(ZC_6H_4SO_2NR^1SO_2R_f)_{2-x}]_n$ , where , R<sub>f</sub> is a C<sub>1</sub>-C<sub>8</sub> perfluoroalkyl, where R<sup>2</sup> is selected from the group consisting of -CH<sub>2</sub>CH<sub>3</sub>, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>, -CH<sub>2</sub>CH<sub>2</sub>OTHP, -C<sub>6</sub>H<sub>4</sub>COOPr, -CH<sub>2</sub>CF<sub>3</sub>, -CH<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>3</sub>, -C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>, -C<sub>6</sub>F<sub>5</sub>, and mixtures thereof, Z is O or NH, and R<sup>1</sup> is selected from the group consisting of Na, Li, H, and K.

18. The copolymer of claim 17 wherein R<sup>2</sup> is -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, and Z is -O-.

19. The copolymer of claim 17 wherein R<sup>1</sup> is Na.

20. A method of making a phenoxy sulfonimide functionalized polyphosphazene copolymer of the formula  $[NP(ZR^2)_x(ZC_6H_4SO_2NR^1SO_2R_f)_{2-x}]_n$ , where , R<sub>f</sub> is a C<sub>1</sub>-C<sub>8</sub> perfluoroalkyl, where R<sup>2</sup> is selected from the group consisting of -CH<sub>2</sub>CH<sub>3</sub>, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>, -CH<sub>2</sub>CH<sub>2</sub>OTHP where THP is tetrahydropyranl, -C<sub>6</sub>H<sub>4</sub>COOPr, -CH<sub>2</sub>CF<sub>3</sub>, -CH<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>3</sub>, -C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>, -C<sub>6</sub>F<sub>5</sub>, Z is O or NH, and R<sup>1</sup> is

selected from the group consisting of Na, Li and K, comprising,

reacting  $(\text{PNCl}_2)_n$ , where  $n \geq 3$  with a first amount of compound of the formula  $\text{R}^3\text{R}^2$  where  $\text{R}^3$  is selected from the group consisting of  $-\text{NaO}$ ,  $-\text{LiO}$ ,  $-\text{KO}$ ,  $\text{NH}_2$  or mixtures thereof,  $\text{R}^2$  is selected from the group consisting of  $-\text{CH}_2\text{CH}_3$ ,  $-\text{C}_6\text{H}_4\text{CH}_3$ ,  
5  $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ ,  $-\text{CH}_2\text{CH}_2\text{OTHP}$  where THP is tetrahydropyranyl,  $-\text{C}_6\text{H}_4\text{COOPr}$ ,  $-\text{CH}_2\text{CF}_3$ ,  $-\text{CH}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3$ ,  $-\text{C}_6\text{H}_4\text{CF}_3$ ,  $-\text{C}_6\text{F}_5$ , or mixtures thereof, with a second amount of a compound of the formula  $\text{R}^2\text{C}_6\text{H}_4\text{SO}_2\text{NHSO}_2\text{R}_f$  where  $\text{R}_f$  is a  $\text{C}_1$ - $\text{C}_8$  perfluoroalkyl, where  $\text{R}^2$  is selected from the group consisting of  $-\text{NaO}$ ,  $-\text{LiO}$ ,  $-\text{KO}$ ,  $\text{NH}$  or mixtures thereof, at a first temperature of about  $60^\circ\text{C}$  to about  $200^\circ\text{C}$  to  
10 produce a reaction product,

reacting the reaction product with  $\text{R}^3\text{R}^2$  at a second temperature of  $60^\circ\text{C}$  to about  $200^\circ\text{C}$  at a pressure of about 3.5-4 bar.

21. A haloalkoxy sulfonimide functionalized polyphosphazene of the formula

15  $(\text{NP}(\text{OCH}_2(\text{CF}_2)_4\text{H})_2)_x (\text{NP}(\text{OCH}_2(\text{CF}_2)_4\text{H})\text{OC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f)_{(1-x)}$  where  $\text{R}^1$  is selected from the group consisting of Na, Li, H, and K, and where  $\text{R}_f$  is a  $\text{C}_1$ - $\text{C}_8$  perfluoroalkyl.

22. The haloalkoxy sulfonimide functionalized polyphosphazene of claim 21 where  $\text{R}^1$  is Na.

23. A method of manufacture of haloalkoxy sulfonimide functionalized polyphosphazene of the formula

$[\text{NP}(\text{OCH}_2(\text{CF}_2)_4\text{H})_x (\text{OC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f)_{2-x}]_n$  where  $\text{R}^1$  is selected from the group consisting of Na, Li and K and ,  $\text{R}_f$  is a  $\text{C}_1$ - $\text{C}_8$  perfluoroalkyl, comprising,

25 reacting  $(\text{NPCl}_2)_n$ , where  $n \geq 3$  with an alkali fluoroalkoxide selected from the group consisting of  $\text{NaOCH}_2(\text{CF}_2)_4\text{H}$ ,  $\text{NaOCH}_2\text{CF}_3$ ,  $\text{NaOCH}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3$ ,  $\text{LiOCH}_2(\text{CF}_2)_4\text{H}$ ,  $\text{LiOCH}_2\text{CF}_3$ ,  $\text{LiOCH}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3$ ,  $\text{KOCH}_2(\text{CF}_2)_4\text{H}$ ,  $\text{KOCH}_2\text{CF}_3$ , and  $\text{KOCH}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3$  to displace about 50% of the Cl in the  $(\text{PNCl}_2)_n$ , where

n≥3 to form a first reaction product,

reacting the first reaction product with an alkali phenoxy sulfonimide of the formula  $R^1OC_6H_4SO_2NMSO_2R_f$  where  $R^1$  is selected from the group consisting of Na, Li and K to produce a second reaction product,

5 reacting the second reaction product with an excess of an alkali fluoroalkoxide selected from the group consisting of  $NaOCH_2(CF_2)_4H$ ,  $NaOCH_2CF_3$ ,  $NaOCH_2CF_2OCF_2CF_2OCF_3$ ,  $LiOCH_2(CF_2)_4H$ ,  $LiOCH_2CF_3$ ,  $LiOCH_2CF_2OCF_2CF_2OCF_3$ ,  $KOCH_2(CF_2)_4H$ ,  $KOCH_2CF_3$ , and  $KOCH_2CF_2OCF_2CF_2OCF_3$  to produce a haloalkoxy sulfonimide functionalized polyphosphazene of the formula

10  $[NP(OCH_2(CF_2)_4H)_2]_x(OC_6H_4SO_2NR^1SO_2R_f)_{2-x}]_n$  where  $R^1$  is selected from the group consisting of Na, Li and K and  $R_f$  is a  $C_1$ - $C_8$  Perfluoroalkyl,.

24. A blend of sulfonimide functionalized polyphosphazene comprising a sulfonimide functionalized polyphosphazene and another polymer selected from the group  
15 consisting polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PDVF), polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP), polystyrene (PS), polybutadiene (BR), polyvinylidene chloride (VDC), polymethyl methacrylate (PMMA), polyvinyl alcohol (PVAL), polyvinyl acetate (PVA), polyphenylene oxide (PPO), polyether ether ketone (PEEK), polyethylene terephthalate (PET), polybutylene  
20 terephthalate (PBT), polycarbonate (PC), polyether sulfone, polybenzimidazoles (PBI), polydimethyl siloxane, polyphenylene sulfide (PS), polypyrrole, polyphenylene, polyaniline, poly(bis(pentoxy)phosphazene), poly(bis(phenoxy)phosphazene), poly((methoxyethoxyethoxy)(m-methyl phenoxy)phosphazene), styrene-acrylonitrile copolymers (SAN), Acrylonitrile-butadiene-styrene terpolymers (ABS) and ethylene-  
25 methacrylic acid copolymer.

25. A blend of claim 23 where the non-phosphazene polymer is polyvinylidene fluoride.

26. A composition comprising a sulfonamide functionalized polyphosphazene polymer and an additive selected from the group consisting of examples such as additives such as carbon black, graphite, platinum, ruthenium, silica, montmorillonite, clay, titanium dioxide, zirconium oxide, phosphoric acid, phosphotungstic acid, silicomolybdic acid, phosphomolybdic acid, salts such as  $\text{CF}_3\text{SO}_2\text{NLiSO}_2\text{CF}_3$ , hexaphenoxycyclotriphosphazene, di(m-methylphenoxy)tetra(trifluoroethoxy)cyclotriphosphazene, plasticizers such as methanol, ethanol and hexane, cross-linkers such as diamines.
27. A membrane comprising a sulfonimide functionalized polyphosphazene of the formula  $[\text{NP}(\text{OC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f)_x(\text{OC}_6\text{H}_4\text{CH}_3)_{2-x}]_n$ , where  $\text{R}^1$  is Li, Na, K, or H and  $\text{R}_f$  is a  $\text{C}_1$ - $\text{C}_8$  perfluoroalkyl.
28. A membrane comprising a sulfonimide functionalized polyphosphazene of the formula  $[\text{NP}(\text{ZR}^2)_x(\text{ZC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_3)_{2-x}]_n$ , where  $\text{R}^1$  is Li, Na, K, or H, Z is O or NH, and  $\text{R}^2$  is an alkyl, aryl, fluorinated alkyl, perfluorinated alkyl, fluorinated aryl, functionalized alkyl or functionalized aryl and  $\text{R}_f$  is a  $\text{C}_1$ - $\text{C}_8$  perfluoroalkyl.
29. The membrane of claim 26 wherein the polyphosphazene is cross linked.
30. The membrane of claim 27 wherein the polyphosphazene is cross linked.
31. The membrane of claim 28 wherein the polyphosphazene is cross linked.
32. A fuel cell comprising a membrane of a polyphosphazene of the formula  $[\text{NP}(\text{ZR}^2)_x(\text{ZC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f)_{2-x}]_n$ , where  $\text{R}^1$  is Li, Na, K, or H, Z is O or NH, and  $\text{R}^2$  is an alkyl, aryl, fluorinated alkyl, perfluorinated alkyl, fluorinated aryl, functionalized alkyl or functionalized aryl,  $\text{R}_f$  is a  $\text{C}_1$ - $\text{C}_8$  perfluoroalkyl, and where the

polyphosphazene is cross linked or uncross-linked.

33. A fuel cell comprising a membrane of a polyphosphazene of the formula  
[NP(OC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NR<sup>1</sup>SO<sub>2</sub>R<sub>f</sub>)<sub>x</sub>(OC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2-x</sub>]<sub>n</sub>, where R<sub>f</sub> is a C<sub>1</sub>-C<sub>8</sub> perfluoroalkyl, where  
5 the polyphosphazene is cross linked.

34. A method of making a lithiated phenoxy sulfonimide functionalized  
polyphosphazene [NP(OR<sup>5</sup>)<sub>x</sub>(OC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NLiSO<sub>2</sub>R<sub>f</sub>)<sub>2-x</sub>]<sub>n</sub> where R<sub>f</sub> is a C<sub>1</sub>-C<sub>8</sub>  
perfluoroalkyl and where R<sup>5</sup> is an oligo-oxy substituent selected from the group  
10 consisting of -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>, -CH<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>3</sub>, -  
CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> comprising,

forming an aqueous, acidic solution of [NP(OR<sup>5</sup>)<sub>x</sub>(OC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NHSO<sub>2</sub>R<sub>f</sub>)<sub>2-x</sub>]<sub>n</sub> and  
subjecting the solution to dialysis against a LiCl solution.

15 35. The method of making the copolymer in claim 34 where R<sup>5</sup> is  
-OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> and the polyphosphazene has the formula  
[NP(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>x</sub>(OC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NLiSO<sub>2</sub>R<sub>f</sub>)<sub>2-x</sub>]<sub>n</sub> where R<sub>f</sub> is a C<sub>1</sub>-C<sub>8</sub>  
perfluoroalkyl.